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Coefficients of Expansion

A VALUABLE addition to the data available on the coefficients of expansion of certain pure metals and carbon steels is contained in a paper by H. Esser and H. Eusterbrock.[1] Their measurements were made in an improved form of dilatometer designed to avoid what they regard as possible sources of error in the Chevenard dilatometer, and describe as defects of construction and procedure, and insufficient precaution against detrimental heat transfer. The new type of dilatometer which they devised is independent of mechanical lever action, and is claimed to be substantially free from the known sources of error. Its great sensitivity enabled very short test pieces to be used.

With this dilatometer the coefficient of linear expansion of a number of metals was determined at 50 deg. intervals from 0 deg. Cent. up to the vicinity of the melting point or up to 1000 deg. Cent., if the melting point was higher. Very full data are recorded, for which the original must be consulted, but indications of the results are given here, and some points of interest which arise are discussed.

The following values were obtained for the true coefficient of expansion at a temperature t deg. Cent. of some of the common metals expressed in the form

$$\alpha = \alpha_0 + a\,t + b\,t^2,$$

α_0 being the true coefficient of expansion at 0 deg. Cent.

Values of $10^6\alpha$

Gold	$14{\cdot}146 + 0{\cdot}0031696\,t + 0{\cdot}000003279\,t^2$
Platinum ...	$8{\cdot}9877 + 0{\cdot}0021304\,t + 0{\cdot}0000003768\,t^2$
Silver	$19{\cdot}494 + 0{\cdot}0020758\,t + 0{\cdot}000007125\,t^2$
Copper ...	$16{\cdot}733 + 0{\cdot}005252\,t + 0{\cdot}00000273\,t^2$
Aluminium...	$23{\cdot}417 + 0{\cdot}009658\,t + 0{\cdot}000013965\,t^2$
Magnesium...	$25{\cdot}003 + 0{\cdot}016602\,t + 0{\cdot}000003975\,t^2$

These values are reproduced as given in the paper, though it appears to be extremely doubtful if such a high degree of accuracy as they imply was actually attained.

ALUMINIUM

It may be of interest to compare the direct dilatometric results of Esser and Eusterbrock with recent determinations by A. J. C. Wilson[2] of the coefficient of expansion of aluminium from lattice spacings measured as a function of temperature by means of the high-temperature Debye-Scherrer X-ray camera. Instead of the usual parabolic (or almost linear) relation, Wilson found an inflection in the curve corresponding to an initial rapid increase, and then a slower increase in α with rise in temperature. Wilson's curve was S-shaped, being above the mean straight line at 100 deg. Cent., and below it at 300 deg. Cent., these departures being stated to be well beyond the experimental error. The expansion-temperature curve of Esser and Eusterbrock did not show any sign of such an irregularity. The values of the true coefficient of expansion at various temperatures obtained by the two different methods are shown in the following table :—

Value of $10^6\alpha$ *for Pure Aluminium*

$t°$.	Wilson.	E. and E.
0	22·0	23·41
100	25·4	24·46
200	26·5	25·78
300	27·8	27·36
400	29·9	29·20
500	32·5	31·31
600	35·5	33·67
650	37·2	—

Wilson used aluminium over 99·99 per cent. pure ; no details as to its condition or preliminary heat treatment are given. Esser and Eusterbrock worked with Hoopes aluminium (99·87 per cent. aluminium), which had been annealed for two hours at 620 deg. Cent., and slowly cooled. Their results agree to within 1 per cent. with the standard value for pure aluminium adapted by the Aluminum Company of America,[3] viz.:—

$$23{\cdot}22 + 0{\cdot}00934\,t + 0{\cdot}0000234\,t^2.$$

There is some lack of agreement in absolute values obtained by other investigators who have made direct measurements of the coefficient of expansion of aluminium, but none of the results gives an indication of an S-shaped curve, nor, so far as is known, has anyone obtained a value as low as 22·0 at 0 deg. Cent.

IRON AND IRON-CARBON ALLOYS

The values of the coefficients of expansion of carbonyl iron, electrolytic iron with 0·004 per cent. and with 0·01 per cent. of carbon, and of iron-carbon alloys made from carbonyl iron have been determined by Esser and Eusterbrock at intervals of 50 deg. or less from 18 deg. to 1000 deg. Cent., and are tabulated in detail. A number of points of interest arise out of the results.

The mean coefficient of expansion of carbonyl iron and of the electrolytic irons is very similar from 18 deg. to 100 deg. Cent. ($10^6\alpha_m = 12{\cdot}10$, 12·20, and 12·16 respectively), but the true coefficient, which in all cases attains a maximum at 525 deg. Cent., reaches a higher value in the carbonyl iron than in the other two ($10^6\alpha$ at 525 deg. = 16·36, 15·86, and 15·78 respectively). Above that temperature the value falls to a sharp minimum at Ac_2 and then rises again. The temperature of the A_2 point was the same in all three samples, but the A_3 points varied.

The following temperatures in deg. Cent. were observed in heating and cooling :—

	Ac_2.	Ac_3.		Ar_3.		Ar_2.
		Start.	End.	Start.	End.	
Carbonyl iron (C trace)...	770	865	918	884	858	769
Electrolytic iron—						
(C = 0·004 per cent.) ...	769	934	945	922	916	767
(C = 0·01 per cent.) ...	770	917	925	903	895	770

The Ac_3 for electrolytic iron was appreciably higher than for carbonyl iron, and there was a smaller lag in cooling.

The mean coefficient of expansion of the iron-carbon alloys between 18 deg. and 100 deg. Cent. diminished with increase in carbon content, thus :—

Carbon, per cent.	$10^6\alpha_m$ (18–100 deg.).	Carbon, per cent.	$10^6\alpha_m$ (18–100 deg.).
Nil	12·10	0·64	11·01
0·13	11·96	0·93	10·54
0·26	11·75	1·12	10·34
0·47	11·58		

The true value of $10^6\alpha$ reached a maximum at about 525 deg. to 650 deg. Cent., according to the carbon content, and fell to a minimum at Ac_1. The cause of this maximum is not clear. The authors suggest that it may be connected with the irregularity observed by Carpenter and Keeling at 575 deg. to 625 deg. Cent., that it may be related to some magnetic property, or that it may be due to the beginning of pearlite dissolution or the formation of γ-iron. An explanation which involved the presence of carbide would not, however, explain the fact that the maximum is shown by pure iron. The effect of the magnetic transformation of iron carbide was an arrest in the rate of change of α at between 195 deg. and 210 deg. Cent. There was slight evidence of it in the alloy with 0·47 per cent. carbon, and it was shown clearly in that with 0·64 per cent. carbon and above, being slightly displaced to a higher temperature by increasing carbon content.

One further feature which is shown by the results is the volume change which occurs at the critical range. The change of length measured by the vertical distance between the α-iron and γ-iron lines in the dilatometric record decreases continuously with increase in carbon content from about 0·37 per cent. to about 0·15 per cent. of the length at 18 deg. Cent. The actual change of length from beginning to end of the transformation is less than this, as it occurs over a temperature range in which part of the contraction is being neutralised by the normal expansion. Hence the actual contraction is least when the critical range is most extensive, *e.g.*, in low-carbon steels, and it is highest when the transformation range approximates to a constant temperature, *e.g.*, in pure iron or in the eutectoid composition. Values of the length change occurring over the critical range are given in the following table :—

Carbon, per cent.	Change of length during the $\alpha \rightleftarrows \gamma$ transformation (percentage of length at 18 deg. Cent.).			
	Ac_1.	Ar_1.	Ac_3 or Ac_1+Ac_3.	Ar_3 or Ar_1+Ar_3.
Nil	—	—	0·293	0·339
0·13	0·019	0·003	0·072	0·122
0·26	0·044	0·021	0·154	0·162
0·47	0·085	0·040	0·157	0·190
0·64	0·109	0·082	0·151	0·186
0·93	0·160	0·158	—	—
1·12	0·150	0·135	—	—

The percentage volume changes are, of course, about three times the above values.

The paper contains an extensive collection of data, which, as indicated in the foregoing account of its contents, may be useful in many connections.

REFERENCES

[1] *Archiv für das Eisenhüttenwesen*, 1940–41, 14, 341.
[2] Proc., Physical Soc., 1941, 53, 235.
[3] *Metals and Alloys*, 1938, 9, 189.

American Work on the Corrosion of Duralumin

WHEN aluminium-rich alloys of the duralumin type were first used in aircraft construction there occurred numerous instances of extremely rapid corrosion accompanied by embrittlement. Investigations were begun at the U.S. Bureau of Standards, Washington (as well as at many other centres in different countries), to develop methods for producing and determining the causes of this corrosion embrittlement and on this basis to evolve methods for its elimination or prevention. Early studies of such variables as chemical composition, heat treatment and ageing of the alloys were successful in these two respects. The efficiencies of various oxide coatings, particularly in combination with organic or paint coatings, were next studied. The corrosion of aluminium alloys when in contact with each other or with dissimilar metals or when joined by rivets and welds is also being investigated.

This work and many other activities in connection with the corrosion of metals used in aircraft are summarised, with full references to the publications in which further details appear, by W. Mutchler[1] in the Bureau of Standards *Journal of Research*. Reference is made in this summary not only to the aluminium alloys but to magnesium alloys and stainless steels, but in the present brief note upon the work, only the duralumin type of alloy will be dealt with in detail.

The general plan of investigation was the same for all materials. Tensile bars, strips or large panels were exposed to accelerated tests in the laboratory, to the weather or to tide water conditions of corrosion and the corroded specimens from each set were removed at progressive intervals for test. Each corroded specimen was photographed and then broken in a tensile test. Differences in the tensile properties from those of uncorroded specimens (stored in a dry atmosphere in sealed containers in the laboratory) served as an indirect measure of the corrosion. Microscopic examination was made of sections of the tested specimens to determine the nature of the corrosive attack and measurements were made of the depth and extent of its penetration. Permanent records of the corrosive attack were made by a special method developed for the purpose.[2] The majority of the accelerated laboratory corrosion tests were conducted either by intermittent immersion (one minute in a solution of 9 parts normal sodium chloride and 1 part commercial hydrogen peroxide, followed by fourteen minutes in air) or in a salt spray or mist of 20 per cent. sodium chloride solution. An apparatus was designed to permit flexural stressing of sheet specimens in order to study the effect of the combined action of stress and corrosion.

The corrosion of alloys of the duralumin type was

found to be of two distinct types, surface pitting and intercrystalline penetration, and the rate at which the material is cooled from the solution-treatment temperature of approximately 500 deg. Cent. is very important in determining the character of the corrosion which may occur. Corrosion of material that has been cooled relatively slowly by quenching in hot water to minimise distortion is mostly confined to the grain boundaries and may penetrate rather deeply without leaving any marked evidence of corrosion on the surface. Corrosion of this type may be very damaging to the ductility and strength of the material, especially of sheets. The same alloy, however, if cooled more quickly, by quenching in cold water, is practically immune to the intercrystalline type of corrosion, though its initial tensile strength and other properties do not differ essentially from those produced by quenching in hot water. Any corrosion that occurs is generally of the pitting type, which has a much less damaging effect on the tensile strength, ductility and other physical properties. The damage to the physical properties of duralumin by corrosion varies with the intensity of the intercrystalline attack. Material with only traces of intercrystalline attack may be damaged no more severely than that corroded by pitting.

Tests illustrating these two types of corrosion are quoted by H. L. Logan.[3] Identical specimens from a single sheet were cooled from the solution heat treatment temperature by quenching in water at 94 deg. Cent. and 26 deg. Cent., respectively, and were examined after immersion for equal periods in a corroding solution. The more slowly cooled material showed severe attack along the grain boundaries. Its ductility as measured by the elongation (on a 2in. gauge length) of the specimen broken in tension was reduced from 21 per cent., which was characteristic of the uncorroded condition, to 4·5 per cent. Similarly, the ultimate strength was reduced from 29·5 tons per square inch (in the uncorroded condition) to 17·9 tons per square inch. The companion specimen that was cooled rapidly by quenching in water at room temperature exhibited only the pitting type of corrosion. The elongation of this specimen after corrosion was 9·4 per cent. and the ultimate tensile strength was 25·7 tons per square inch.

The amount of corrosion was assessed by the Bureau of Standards by micrographic examination of the depth of penetration of the damage and by the strength-ductility index, *i.e.*, the percentage ratio of the product of the tensile strength and elongation of the corroded specimen to the corresponding average product for the uncorroded specimens. It was found on examination of a large number of results that the value of this product tends to be almost proportional to the ductility and was not closely related to the tensile strength of the corroded material.

The method of testing outlined above is a time-consuming process and necessitates the cutting of specimens from the article. A more rapid and non-destructive test has long been sought. The electrode potential of an alloy of the duralumin type varies with the heat treatment and particularly with the rate at which the alloy has been cooled after the solution heat treatment. Suggestions have been made by F. P. Somers, of the Naval Aircraft Factory, Philadelphia, and by E. H. Dix, jun., of the Aluminum Company of America, that potential measurements should be used to predict the type of corrosion to which the material may be susceptible. This method has been developed and demonstrated to be effective by H. L. Logan.[3] He used commercial sheet material conforming with the chemical specifications referred to below as 17 S and 24 S and also some duralumin of German origin.

	17 S, per cent.	24 S, per cent.
Copper	4·0	4·4
Magnesium	0·5	1·5
Manganese	0·5	0·5
Iron (max.)	1·0	0·5
Silicon (max.)	0·8	0·5
Total other elements (max.)	0·38	0·38
Aluminium	Remainder	

The potential measured was the E.M.F. of a cell in which a small area (0·8 to 1·0 square centimetre) of the metal surface was in contact with a saturated solution of potassium chloride which in turn was connected to a standard calomel electrode. The potential measurements could be made most accurately by charging a condenser by means of the cell and discharging it through a calibrated ballistic galvanometer. The relative potential could more readily be determined by setting a potentiometer at an expected value and determining from the galvanometer deflection whether the actual potential was greater or less than that chosen. The results most consistent with those of the accelerated corrosion tests were obtained by recording the galvanometer deflection after a relatively steady state had developed, which was usually in from ten to twenty seconds after connection had been made between the specimen and the calomel electrode. As in all cases the aluminium alloy was negative to the mercury of the half cell, the electrode potential is reported as negative. It was found to be most important that the surface film on the metal tested should be completely removed by fine emery, and no electrode potential measurements were made until at least six minutes after the surface preparation had been completed.

It was found that all specimens which gave an electrode potential more electronegative than —0·672 volt were susceptible to intercrystalline corrosion, usually severe, and all with potentials less than —0·648 volt were immune. A potential of —0·657 volt at 25 deg. Cent. was selected as the critical value. If the potential (checked by a second set of readings with a freshly prepared surface) was more negative than this, the specimen was classified as susceptible to intercrystalline corrosion in some degree. Of all the 700 specimens studied between 85 and 90 per cent. were correctly classified. It is not possible to predict the degree of intercrystalline attack from potential measurements, but the prediction of susceptibility is much more certain for specimens liable to severe attack than for those which are only slightly affected. The most likely sources of error were irregularity of heat treatment of sheets, so that the part tested was not representative of the whole, and incorrect preparation of the surface. Differences of copper content were not an appreciable source of error.

Potential measurements, as a means of predicting susceptibility of aluminium alloys of the duralumin type to intercrystalline corrosion, have thus been shown to be a rapid and reliable method of checking heat treatment, but they can only be made by persons of some scientific training and experience. If the method is further substantiated it should be possible, without destroying the structure, to predict with a high degree of certainty whether material in a structure such as an aeroplane wing is susceptible to intercrystalline corrosion. The degree of susceptibility will not be revealed, but, on the other hand,

material most liable to severe intercrystalline attack is least likely to escape detection. The author makes no claim that potential measurements can replace the present accelerated corrosion tests, but provides encouraging evidence in support of the view that such measurements will prove to be of increasing value and interest in the future as a basis for the prediction of immunity or susceptibility to intercrystalline corrosion.

REFERENCES

[1] Bureau of Standards, *Journal of Research*, July, 1940, Vol. 25, page 75.

[2] "Trans.," Amer. Soc. Metals, 1938, 26, 279.

[3] Bureau of Standards, *Journal of Research*, Sept., 1940, Vol. 25, page 315.

The Elastic Modulus of Solid Solutions

IT is well known that the elastic modulus of steel is almost unaffected by heat treatment, the value of E for the martensitic condition being lower than that for the pearlitic condition by about 5 per cent. in high-carbon steels. P. Chevenard and A. Portevin[1] found that the modulus of the aggregate of iron and iron carbide varied linearly with composition and that the modulus of solid solutions like Ag-Au, Cu-Ni and within limits Cu-Al, Cu-Zn, &c., showed little deviation from the linear relation. Z. Nishiyama,[2] in determining E for a series of solid solutions, found that its value generally diminished with increasing atomic distance in the alloy. It is, of course, not related in any way to hardness. L. Guillet, jun., found a linear relation between modulus and composition in alloys consisting of two phases, and an approximately linear relation in solid solutions. Intermetallic compounds fall into two groups: those with metallic characteristics, *e.g.*, CuZn, $CuAl_2$, &c., in which the modulus agreed with that calculated by the law of mixtures; and (2) the homopolar compounds, such as Cu_5Zn_8, $Cu_{31}Sn_8$ and Cu_9Al_4, in which the modulus was considerably higher than the value calculated in this way, and in some cases higher than that of either constituent. Examples were:—

Compound.	Value of E, kg. per sq. mm.	Calculated by rule of mixtures.
Cu_9Al_4	16,850	11,750
Cu_5Zn_8	14,800	9,700
$Cu_{31}Sn_8$	12,150	9,850

In connection with a recent paper by Professor C. Benedicks[3] on "The Elasticity of Solid Solutions," special interest attaches to Guillet's conclusion that the modulus of elasticity undergoes a 40 per cent. diminution by quenching when the effect of this treatment is to preserve a supersaturated solid solution. For example:—

Alloy.	Modulus of elasticity, kg. per sq. mm.
Cu+13% Al. ...	Annealed ($\alpha+\delta$) 13,300 Quenched (β) 8300
Cu+25% Sn ...	Annealed ($\alpha+\delta$) 11,400 Quenched (β) 6820

In general a supersaturated solid solution is characterised by a lower value of E than the alloy in the equilibrium condition. Professor Benedicks proceeds to discuss the reason for the diminution of the modulus. In considering the lattice structure of solid solutions he indicates that the atoms are not, as in pure metals, arranged in straight lines in the lattice, but are displaced by the action of the substituting atoms on to zigzag or undulating lines. The lattice undulations offer a greater resistance to slip and so result in greater hardness and higher elastic limit than the pure metals. On the other hand, resistance to an elastically reversible deformation should be less: in stretching a smoothing out of the undulations will tend to occur and in compression

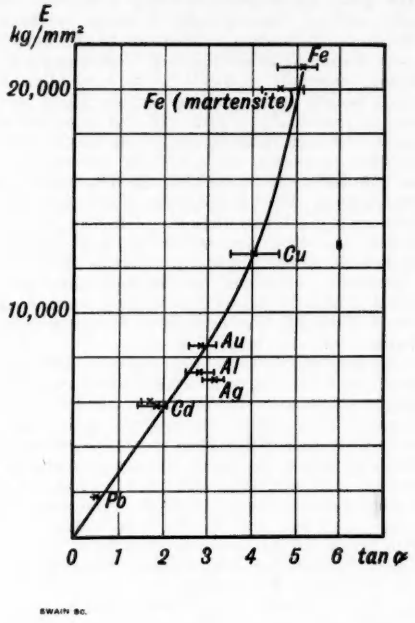


FIG. 2—*Calibration Curve of the Chevenard Machine*

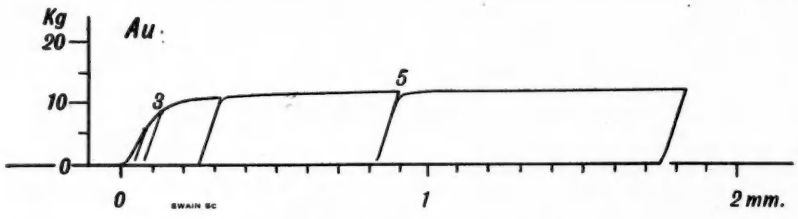


FIG. 1—*Load-extension Record for Gold*

they will become intensified. The lowering of E can only be expected to occur for small degrees of deformation. If considerable deformation is applied, E tends to approach the normal value given by an undeformed lattice. The condition is illustrated by the analogy of two metal wires, one straight and the other undulated. Under the same small load the extension of the latter will be greater, *i.e.*, the undulated wire will show the lower apparent value of E. The idea is similar to that put forward by E. Mack, jun.,[4] to explain the elasticity of rubber, viz., the pre-existence of folded chains of atoms, which pass, on loading and unloading, from the retracted to the extended form and *vice versâ*.

In the course of an investigation of the electrochemical potential of the gold-cadmium alloys, A. Olander[5] referred to alloys in the β region in the following terms :—" The β alloys with less than 50 atoms per cent. of cadmium were elastic, this property having a sharply marked maximum at 47·5 atoms per cent. A 1 mm. diameter wire of this alloy was so elastic that it almost reminded one of rubber." This property is shown only by alloys within a narrow interval of about 1 per cent. round the composition given above.

Professor Benedicks has carried out some tests on the " Olander alloy " in the Chevenard micro machine[6] for the photographic recording of stress-strain relations on test pieces 2 mm. in diameter and 10 mm. acting length. Successive loading and unloading of the specimen produced a diagram like Fig. 1, which gives the stress-strain relation for gold. By means of a calibration curve (Fig. 2), in which the tangent of the inclination to the base line is plotted against the known value of E for certain metals, the elastic modulus of the alloys tested could be quickly determined from the slope of the load-extension lines. When E is low the relation between E and tan α is linear, but with higher values the curve departs from the straight line, presumably because of elastic deformation in the holders for the test piece. The results of a series of tests on alloys of slightly varying composition in the neighbourhood of 47·5 atoms per cent. (34·1 per cent. by weight) of cadmium are given in Fig. 3. The compound AuCd (36·3 per cent. by weight of cadmium) gave a normal result. The test was soon over, as the test piece broke, but the load lines all gave nearly the same value tan α = 2·46, which, according to Fig. 2, corresponds to E = 7000 kg. per sq. mm., a value slightly lower than the mean of gold and cadmium (7700 kg. per sq. mm.). Another test with somewhat lower cadmium (Fig. 3*b*) gave 5400 with an increasing amount of hysteresis on loading and unloading. Fig. 3*c* represents a third test on material which was made for AuCd, but which must have lost some cadmium. An alloy which should

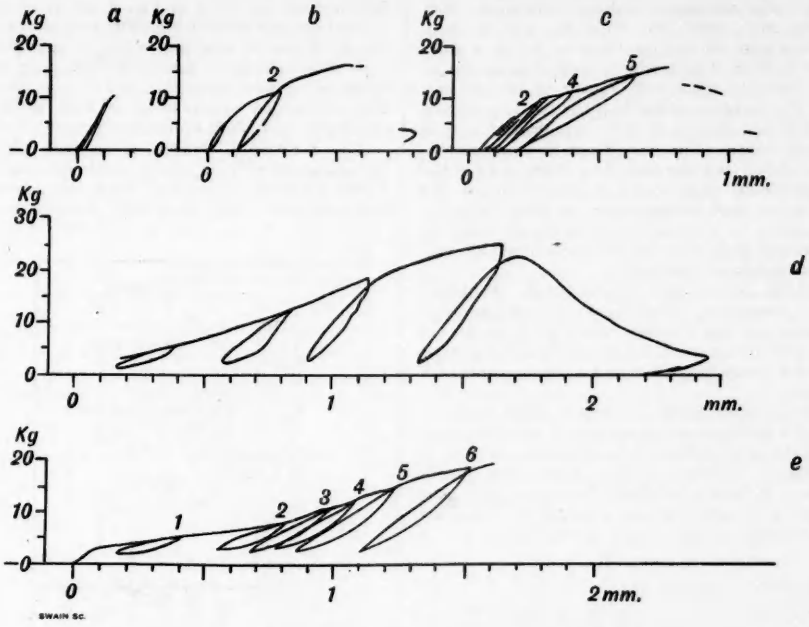


FIG. 3—*Load-extension Records for Gold-cadmium Alloys*

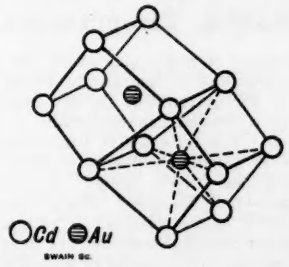


FIG. 4—*Lattice Structure of AuCd*

be identical with Olander's (34·1 per cent. cadmium by weight) gave the record 3*d*. The first loading shows a very low value of E (approximately 2200 kg. per sq. mm.), but this low initial value was increased by loading and unloading, so that the last cycle before the specimen broke gave a value of 5000. Another test piece of the same alloy, but probably with a slightly lower cadmium content, gave the record 3*e*. Its general character is the same as 3*d*, but the curves were flattened and the test piece did not break. The successive values of E were 1900, 2300, 2500, 2800, 3000, and 3100 kg. per sq. mm. These alloys were shown by Olander to be a solid solution of gold in AuCd, which itself was shown to possess a strongly deformed (zigzag or undulating) lattice of the caesium chloride type (body centred) with 8 cadmium atoms at the corners and a gold atom at the centre (Fig. 4). There is some microscopical evidence that the solubility of the gold in the β phase (above 267 deg. Cent.) is greater than in the β′ phase below that temperature, so that the alloy quickly cooled to ordinary temperatures may be supersaturated and thus be characterised by still greater deformation of the lattice.

The elastic behaviour agrees with Professor Benedicks' theoretical forecast, which assumes that the disturbances in the lattice which give rise to the low value of E for the small deformations are smoothed out when the strain is greater and a higher value of E is obtained.

While this investigation does not claim to be of more than a preliminary character, it indicates that there may be solid solutions in analogous regions in other systems showing similar anomalous elastic behaviour. It seems unlikely however, that any practically useful alloy will be affected by the possibility of showing an abnormally low modulus.

REFERENCES

[1] *Comptes Rendus*, 1925, 181, 780.
[2] *Science Reports, Tohôku Imperial Univ.*, 1926, 18, 359.
[3] *Jernkontorets Annaler*, 1940, 124, 225.
[4] *Journal*, American Chem. Soc., 1934, 56, 2757.
[5] *Journal*, American Chem. Soc., 1932, 54, 3819; *Zeit. für Kristallographie*, 1932, (A) 83, 145.
[6] *Bull.*, Soc. d'Encour. pour l'Ind. Nat., 1935, p. 59.

Tensile Properties of Iron at Raised Temperatures

THE influence of impurities or of the minor constituents of iron and of dead-mild steel on the tensile properties of the material at slightly raised temperatures has been studied experimentally and discussed in a paper on " The Influence of Impurities in Iron on the Change in Tensile Properties of Normalised Soft Steel in the Blue-brittle Range," by W. Eilender, H. Cornelius and P. Menzen.[1] The particular phenomenon studied is the change in properties which occurs over the range of temperature from 20 deg. to 350 deg. Cent. and more precisely within the so-called blue-brittle range of temperature. A typical example of this well-known change in properties is shown in Fig. 1, which refers to an Armco iron remelted in a high-frequency furnace and having the composition shown against steel No. 10 in the table. The tensile strength increases with rise in temperature up to a maximum value at 175 deg. to 225 deg. Cent. and then falls again; the elongation falls to a minimum at 125 deg. to 200 deg. Cent. and then rises again; the reduction of area goes through a similar series of changes, the minimum value being attained at 200 deg. to 225 deg. Cent. The exact amount of rise or fall and the temperatures at which the maximum or minimum occurs will depend upon the conditions of experiment, particularly on the rate of straining. In the tests recorded in Fig. 1, as in all other tests carried out in this investigation, test pieces 10 mm. in diameter and 50 mm. gauge length were used. They were stretched at the rate of 0·5 mm. per minute and were maintained at within ±3 deg. of the required temperature by means of an oil bath with a thermostatically controlled immersion heater.

The behaviour illustrated in this diagram was investigated for over thirty steels containing carbon 0·006 to 0·15, silicon 0 to 0·16, manganese 0·03 to 0·4, sulphur 0·004 to 0·056, phosphorus 0·009 to

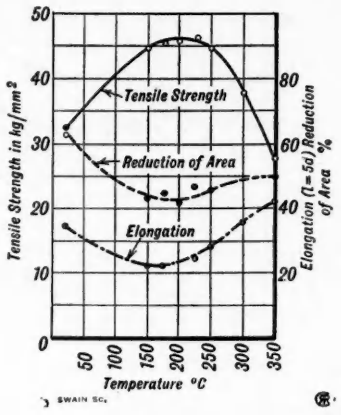
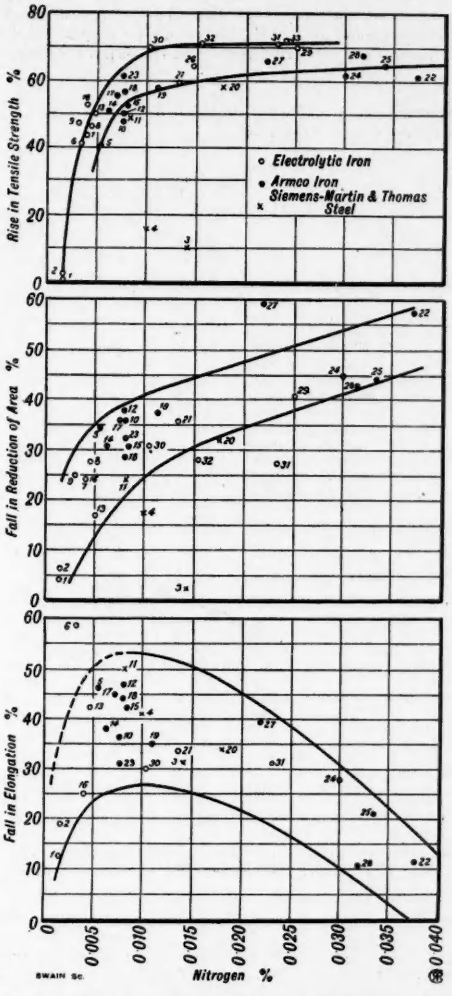


FIG. 1—*Influence of Temperature on the Tensile Properties of Steel* 10 (*Table I*)

0·105, aluminium 0 to 0·08, nitrogen 0·0015 to 0·037, and oxygen 0·0016 to 0·25 per cent. They had been made from electrolytic iron in a magnesite crucible heated in a carbon tube furnace, from Armco iron melted in a basic high-frequency furnace, or commercially in the basic Bessemer converter or open-hearth furnace. A list of the steels is given in a table with details of composition and manufacture, and a record of the maximum change in the properties experienced in the blue-brittle range expressed as a percentage of the values at room temperature. The steels are arranged in order of increasing change in the maximum load in tension which varies over a wide range from nil to 70·7 per cent. The only constituent of the steel which shows any tendency to vary in the same way as the tensile strength is the nitrogen content, which with occasional exceptions increases as the change in tensile strength increases. The changes in each of the properties, tensile strength, reduction of area and elongation, were accordingly plotted against the nitrogen content of the steel in Figs. 2, 3 and 4. The maximum rise in tensile strength showed a rapid increase with increase of nitrogen content up to 0·01 per cent. and then attained a fairly steady value. The increase was greater in steels made from electro-

[1] *Archiv für das Eisenhüttenwesen*, 1940–41, 14, 217.

lytic iron than in those made from Armco iron. Commercial steels Nos. 3 and 4, killed with silicon, fall outside the limits for steel of similar nitrogen contents, whereas the unkilled commercial steels fall into positions approximately normal for their nitrogen content. This might suggest that the lowering of the oxygen content by silicon was the cause of the small



FIGS. 2 TO 4—*Relation between Nitrogen Content and Maximum Rise in Tensile Strength (Fig. 2), Fall in Reduction of Area (Fig. 3), and Fall in Elongation (Fig. 4) of the Steels referred to in Table below in the Blue-brittle Range*

increase in strength, but against this was the fact that some remelted electrolytic iron showing the greatest increase in strength also contained equally low oxygen contents.

The decrease in reduction of area showed a similar dependence on nitrogen content, but the scatter of the results was greater and the distinction between steels made from electrolytic and Armco iron was less marked. Steels 3 and 4 (especially 3) again occupied an anomalous position. The percentage fall in elongation also shows a dependence on the nitrogen content, but the scatter of the results is greater and the curve first rises and then falls again in contrast with the curves for the other properties. The fall in elongation is just as marked in steels made from Armco iron as in those made from electrolytic iron, and the commercial steels all lie within the region of scatter.

It is clear from experiments on rate of straining that the increase in tensile strength in the blue-brittle range is closely related to the phenomenon of strain-age-hardening. Any explanation which meets the facts in one case should be applicable to the other. The change in tensile properties of cold-worked soft carbon steel with time has been attributed to a precipitation process which is acclerated by raising the temperature. In a study of strain-age-embrittlement W. Eilender, H. Cornelius and H. Knüppel[1] found that nitrogen increased the ageing effect considerably, whereas oxygen had no influence. Nitrogen is characterised by increasing solubility in α iron with rise in temperature, and a supersaturated nitrogen-iron solid solution is retained by comparatively slow cooling to room temperatures; but the necessary conditions for hardening by precipitation of oxides are apparently not present in the iron-oxygen system.

The experimental data summarised in the table lead to the conclusion that the nitrogen content of the steel is an important factor in producing the change of properties in the blue-brittle range. It must be remembered that, not only an increase of strength and diminution in ductility, but even an arrest in the fall of strength and in the rise of ductility are a departure from what might be regarded as the normal behaviour of a metal. It therefore appears that a nitrogen content of only 0·0015 per cent. (steels 1 and 2) can exert an influence in checking the fall in tensile strength as the temperature is raised. On the precipitation theory this would require, for the solubility of nitrogen in α iron at 225 deg. Cent., a lower value than was given by W. Köster, who, in reviewing the available data, arrived at the values 0·001 per cent. at 100 deg., 0·005 per cent. at 200 deg., and 0·01 per cent. at 300 deg. Cent.

Aluminium (not intentionally added) was found in steels 6, 14, 25 and 31 to the extent of 0·05 to 0·08 per cent. The aluminium may have been present as nitride or oxide, but the fact that the steels occupied normal positions in Figs. 2 to 4 indicates that it was mainly in the form of oxide, though when the nitrogen content is high it is impossible to draw such a deduction with certainty.

In estimating the effect of oxygen on the behaviour of iron in the blue-brittle range it is necessary to take into account the fact that some of the oxygen will be combined with aluminium, if present. Only nine of the steels were analysed for aluminium and five of them were found to be aluminium-free, while the other four contained 0·05 to 0·08 per cent. A comparison of the steels (divided into groups of steels with similar nitrogen content) on the basis of their total oxygen content reveals no relation between their behaviour in the blue-brittle range and their oxygen content, although the differences between the separate groups again emphasise the influence of nitrogen. Even if the comparison is confined to steels from which aluminium is proved to be absent and to those containing more than 0·07 per cent. of oxygen (this

[1] *Archiv für das Eisenhüttenwesen*, 1934–35, 8, 507.

being the maximum amount which would be combined on the assumption that aluminium content did not exceed 0·08 per cent.) any effect of oxygen in causing the increase in strength in the blue-brittle range is shown to be trivial.

The results contained in the table show that sulphur is without influence on the change in properties in the blue-brittle range. The same applies to phosphorus. The highest phosphorus present in any of the steels was 0·105 per cent., which is considerably below the solubility limit of phosphorus in α iron at room temperature, so that the precipitation of silicon to enable any conclusions to be drawn. The same holds for carbon content. The few steels in which carbon is over 0·03 per cent. seem to show that carbon tends to counteract the influence of nitrogen.

The main conclusion to be drawn from the work of Eilender, Cornelius and Menzen is that nitrogen is the chief cause of the increase in tensile strength of iron and mild steel in the blue-brittle range and that its influence is exerted by precipitation of nitride. It is a well-known fact that the temperature of maximum change in properties can be displaced to a higher temperature by increase in the rate of deforma-

TABLE.—*Chemical Composition of the Experimental Steels and Maximum Change in Tensile Properties in the Blue-brittle Range, Expressed as Percentages of the Values at Room Temperature*

Steel.	Method of manufacture.*	C.	Si.	Mn.	P.	S.	Al.	N_2.	O_2.	Maximum change in the blue-brittle range.		
										Rise in tensile strength.	Fall in reduction of area.	Fall in elongation.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	E	0·007	Trace	n.d.†	0·016	0·018	n.d.	0·0016	0·0154	0	4·3	12·4
2	E	0·009	Trace	n.d.	0·015	0·022	n.d.	0·0015	0·0090	1·5	6·4	18·5
3	Th	0·08	0·16	0·40	0·052	0·021	n.d.	0·014	0·0016	9·1	2·6	31·4
4	SM	0·10	0·11	0·40	0·025	0·023	n.d.	0·010	0·0420	15·0	17·5	41·0
5	A	0·15	0·01	n.d.	0·030	0·056	0	0·0053	0·0081	40·0	34·3	46·6
6	E	0·06	Trace	0·18	0·015	0·017	0·06	0·0033	0·0250	41·0	—	58·7
7	E	0·010	n.d.	n.d.	n.d.	n.d.	n.d.	0·0040	0·0091	43·0	25·0	—
8	E	0·006	n.d.	n.d.	n.d.	n.d.	n.d.	0·0043	0·0720	45·7	27·8	—
9	E	0·009	n.d.	n.d.	n.d.	n.d.	n.d.	0·0030	0·0440	46·4	25·2	—
10	A	0·015	Trace	0·03	0·018	0·036	n.d.	0·0076	0·1620	47·1	35·8	36·8
11	SM	0·08	0·006	0·33	0·025	0·045	n.d.	0·0080	0·0140	48·4	24·3	50·0
12	A	0·012	Trace	0·03	0·022	0·037	n.d.	0·0077	0·200	48·8	37·7	46·6
13	E	0·025	0·06	n.d.	0·014	0·004	n.d.	0·0048	0·0039	49·0	17·1	42·6
14	A	0·010	Trace	0·03	0·105	0·037	0·08	0·0062	0·251	50·0	31·2	37·9
15	A	0·015	Trace	0·03	0·020	0·035	n.d.	0·0081	0·176	54·4	30·8	42·8
16	E	0·03	0·015	0·16	0·014	0·010	0	0·0040	0·017	52·1	24·4	24·8
17	A	0·012	Trace	0·03	0·019	0·040	n.d.	0·0072	0·200	54·5	35·8	44·9
18	A	0·011	Trace	0·63	0·079	0·031	0	0·0077	0·227	55·5	28·6	44·8
19	A	0·012	Trace	0·03	0·027	0·036	n.d.	0·0111	0·184	56·6	37·3	34·8
20	Th	0·07	0·008	0·40	0·087	0·056	0	0·0176	0·017	56·9	31·7	34·0
21	E	0·01	0·028	0·15	0·022	0·010	n.d.	0·0135	0·014	58·6	35·7	33·5
22	AW	0·013	Trace	0·03	0·011	0·048	n.d.	0·0374	0·235	60·0	56·8	11·5
23	A	0·013	Trace	0·10	0·012	0·036	n.d.	0·0077	0·227	60·1	32·1	30·6
24	AW	0·015	Trace	0·04	0·010	0·033	n.d.	0·0301	0·157	60·2	44·8	28·1
25	AW	0·017	Trace	0·03	0·012	0·032	0·05	0·0342	0·190	63·0	44·3	20·9
26	E	0·03	0·02	0·16	0·026	0·010	n.d.	0·0146	0·013	63·2	—	—
27	A	0·025	Trace	n.d.	0·010	0·034	0	0·023	0·085	65·3	59·4	39·6
28	AW	0·014	Trace	0·04	0·012	0·040	n.d.	0·032	0·167	66·2	42·8	11·0
29	E	0·018	0·05	n.d.	0·014	0·018	n.d.	0·025	0·0115	68·3	40·6	—
30	E	0·02	0·028	0·15	0·020	0·022	n.d.	0·0103	0·013	68·5	30·9	30·0
31	E	0·02	0·015	0·11	0·016	0·034	0·08	0·023	0·019	69·7	31·7	27·6
32	E	0·02	0·02	n.d.	0·010	0·015	n.d.	0·0154	0·0085	69·8	28·4	—
33	E	0·015	0·02	n.d.	0·009	0·025	n.d.	0·024	0·015	70·7	—	—

* A = Melted in basic 50-kilo. H.F. furnace from Armco iron; E = melted in magnesite crucible in carbon tube furnace from electrolytic iron; SM = Siemens-Martin (open-hearth) steel; Th = Thomas (basic Bessemer) steel; W = cast in water-cooled mould.

† n.d. = Not determined.

phosphide could only occur locally in regions of marked segregation. Manganese has no influence, not even indirectly through combination with oxygen, which is further evidence against the influence of oxygen. The effect of nitrogen is unaffected by variation in manganese content.

The data are insufficient to throw much light on the influence of silicon. Steels 3 and 4, killed with silicon, show a very small change in tensile properties in the blue-brittle range in relation to their nitrogen content. On the other hand, the changes in steels 13 and 29 with 0·06 and 0·05 per cent. of silicon are considerable. All the remaining steels contained too little

tion. This is claimed by the authors of the paper to fall into line with the precipitation hypothesis. In rapid deformation in the blue-brittle range the time does not suffice for the completion of the precipitation initiated by deformation. With increasing temperature the influence of time becomes relatively less important than the influence of temperature, so that at higher temperatures even during deformation carried out at greater speeds the time suffices for the completion of the decomposition of the supersaturated solid solution. It should be noted that the conclusions drawn may apply only to mild steels in the normalised condition.